SEMI-FINAL REPORT

National Aeronautics and Space Administration
Electronics Research Center
Cambridge, Massachusetts

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IMPURITIES AND INTERFACE
STATES IN THE $SiO_2$/Si
SYSTEM

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/ Semi-Final Report

Impurities and Interface States in the $SiO_2$/Si System

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Contract Monitor: Frank J. Cocca

Principal Investigator: Alan B. Kuper

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## Abstract

Principal new results in this report are:

1. $P_2O_5$ glassing not only getters Na, but also stabilizes $SiO_2$ even at concentrations of Na around $10^{18}$ $cm^{-3}$.

2. A model for instability of Si surface potential has been developed which explains slow drift with field-plate positive followed by fast drift with plate negative in hot-bias MOS tests.

Preliminary results of hydration and radioactive gold experiments are also reported.

# Contents

"Impurities and Interface States in the $SiO_2$/Si System"

Purpose: (1) To understand factors contributing to instability in surface properties of silicon planar devices and (2) to provide information which silicon device engineers can use to improve reliability.

## Introduction

Four months have elapsed since the last report on the grant. During this period main emphasis has been in two areas (1) Passivation against Na impurity by phosphosilicate glass and (2) Theory of impurity charge in MOS oxide.

The former work will be presented this Fall at the 1967 IEEE Reliability Physics Symposium, the latter was presented May 10 to the Electrochemical Society and has been submitted for publication.

Significant conclusions from this work which should provide silicon device engineers with information to improve reliability are:

(1) The $P_2O_5$ glassing process does more than getter Na, it maintains the Si surface stable even with Na concentration around $10^{18}$ $cm^{-3}$ in the oxide.

(2) Theory compared to experiment indicates that relatively slow surface potential shift generally observed in hot-bias is characteristic of Na drift across the oxide. This, and the reason for asymmetry in hot-bias cyclic drift is discussed later in detail.

Two other areas of research are being actively pursued:

(1) Impurity interaction (water species-Na)

(2) Gold effects

Interface States, their origin and interaction with impurities, is the next part of the research program to be investigated.

Phosphosilicate Glass Passivation Against Sodium (W. Smith)

Silicon surface potential under wet-grown oxide was stabilized by growing a phosphosilicate glass layer over the oxide at $900^{\circ}$C. Profiling of glass-oxide contaminated with radioactive $Na^{24}Br^{82}$, and electrical measurements on MGOS capacitors was done. Phosphorus profiles were obtained by activation analysis of $P^{32}$.

Phosphorus concentration profiles are shown in Fig. 1 for glass over oxide as grown for 30 min. at $900^{\circ}$C and for a sample which was heated an additional 30 min. at $900^{\circ}$C in nitrogen.

Penetration of the glass/oxide interface was determined by etch-rate and was found to proceed as time$^{1/2}$ indicating that diffusion of $P_2O_5$ was rate-limiting penetration. The concentration of $P_2O_5$ in the glass was $5\text{-}8 \times 10^{21}$ cm$^{-3}$ in close agreement with the equilibrium concentration obtained from the phase-diagram at $900^{\circ}$C [1, 2]. We note that a substantial amount of Phosphorus diffuses into the $SiO_2$.

In an effort to determine mechanisms by which phosphosilicate glass stabilized the $SiO_2$/Si system, relatively large concentrations of Na were diffused in to the glass/oxide. The technique used to accomplish this was to contaminate the outer surface with NaBr after glassing and then to cover with a polished Si slice during 30 min. diffusion at $900^{\circ}$C. In this way, substantial Na was retained within the oxide. A comparison of contamination before glassing and after glassing for two samples is shown in Fig. 2, indicating that heavier contamination was achieved by the latter technique.

The result of this heavy contamination was however: (1) no C-V flat band voltage shift ($\Delta V$) and (2) no substantial $\Delta V$ at high stress ($200^{\circ}$C, $10^6$V/cm).

Preferential segegration of Na at the glass/oxide interface, found in this work, has been discussed in the last report.

# CONCLUSIONS

The major conclusions of this work are:

1. Phosphosilicate glass grown over silicon dioxide, traps Na and Br in or near the glass.

2. Bulk trapping in the glass is predominant for large Na contamination levels ($> 5 \times 10^{19}$/cc).

3. Bulk trapping in the glass appears to saturate at about 20% of $P_2O_5$ concentration.

4. Beyond this contamination level Na diffuses into the oxide but is electrically inactive as seen by the Si surface.

5. Glass/oxide interface trapping is present and predominates at low Na and Br levels ($< 5 \times 10^{18}$/cc).

The most important conclusion of this work is that the phosphosilicate glass does more than trap impurities. It seems to render impurities electrically inactive in the oxide as well as in the glass. Glassing may alter the structure of the oxide or possibly that of the silicon surface because of appreciable concentrations of phosphorus diffusing through the oxide. This could make electrical stressing ineffectual. Since $P_2O_5$ is a desiccant, and glassing at $900^\circ$C is a drying step, experiments to determine the role of water in this process could be essential.
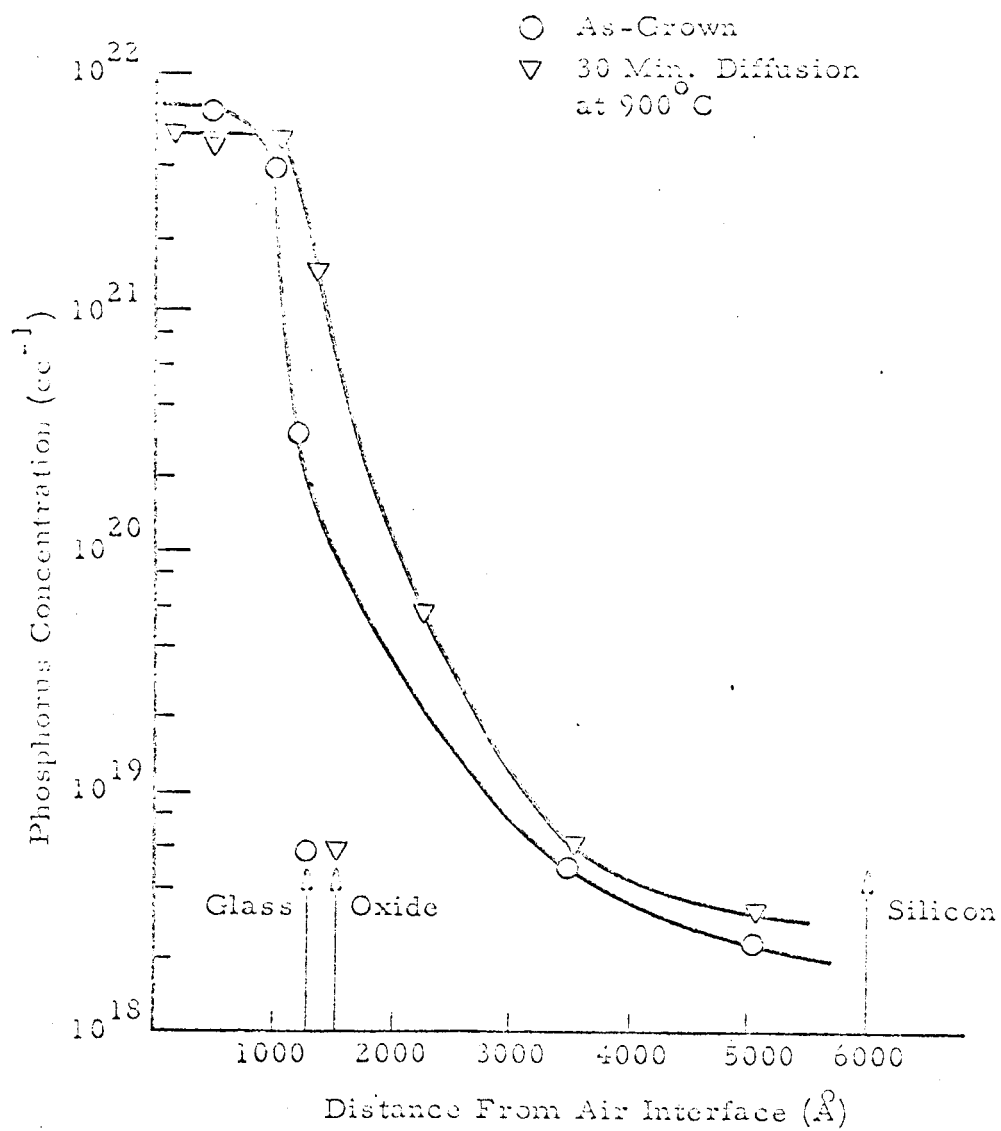
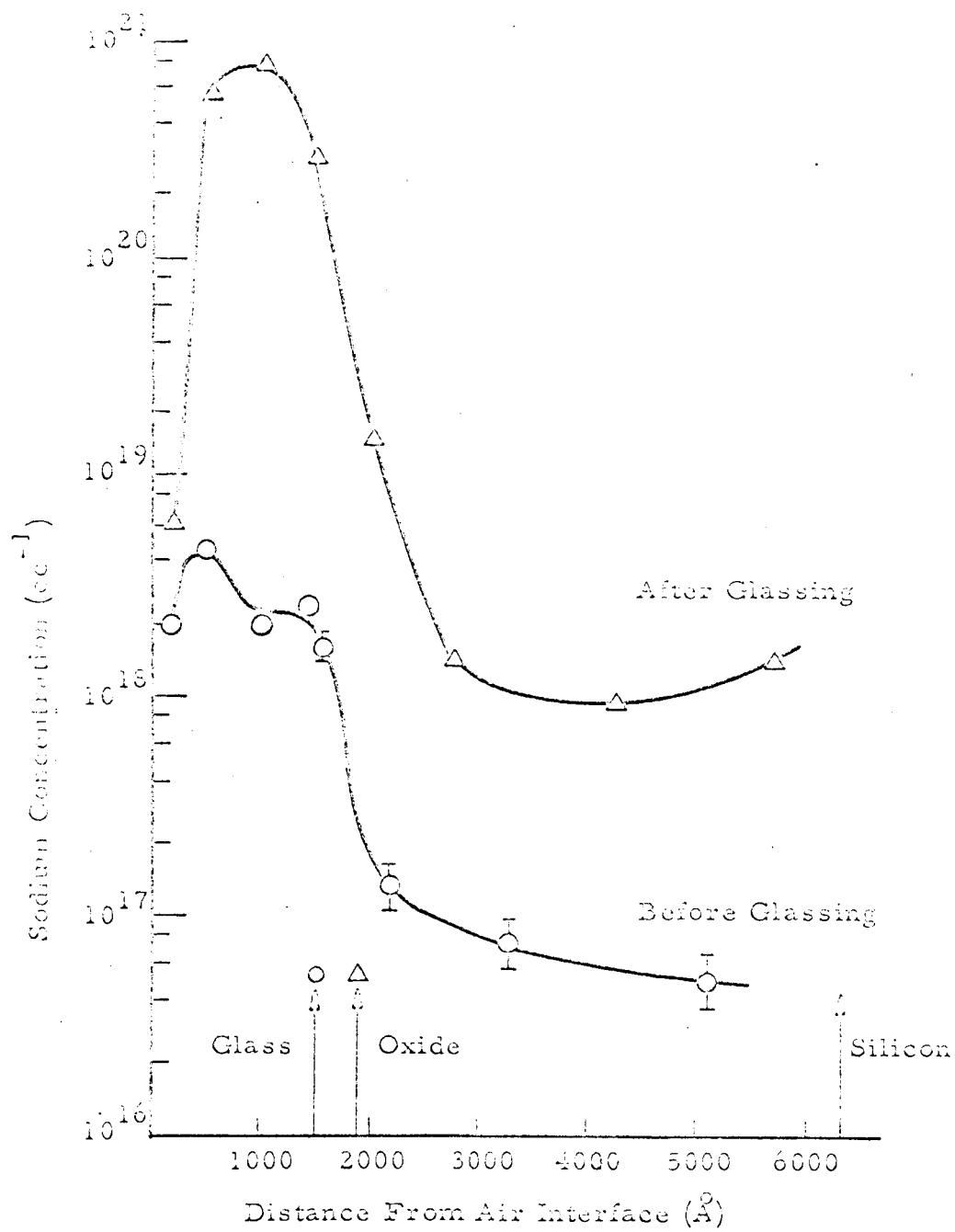Figure 1. Phosphorus Concentration in Glass/Oxide Films

Figure 2. Comparison of Samples Contaminated
Before and After Glassing at $920^{\circ}$C

## Theory of Impurity Charge in MOS Oxide (H. P. Caban-Zeda)

Steady-state distribution, $N(x)$, of charged impurities in homogeneous oxide in MOS is calculated by solving the Continuity equation and Poisson's equation assuming that neutral impurity is initially at M surface and moves between blocking electrodes. Three cases are solved: (1) cation mobile, fully ionized, (2) cation mobile, recombining with anion near the M/O interface, (3) anion and cation both mobile. Bias applied, plates shorted, and plates floating are considered.

Results are compared with experimental $N(x)$ in $SiO_2$ on Si obtained by radiotracer analysis after diffusion and drift of Sodium (Na).

Although the experiments do not satisfy the assumptions of the theory (in particular the observed distributions are not steady-state), comparison of theory with experiment suggests:

1. Pile-up of Na in the oxide at the Si is due in part to charged $Na^+$ paired with image charge in the Si surface.

2. Most of the Na in the oxide is effectively neutral.

3. NaBr impurity distribution results from association-dissociation with diffusion and drift rather than from unassociated ions.

The conclusion that most Na in the oxide is effectively neutral, is consistent with other experimental results.

These conclusions in turn suggest a model to explain observed slow-in/fast-out kinetics of hot-bias electrical drift in MOS. In this model, instability is due to Na. In-drift of Na across the oxide is rate-limited by bulk trapping (association) within the oxide; out-drift is drift of $Na^+$ from the Si interface into the oxide and is relatively independent of oxide state.

The mathematical development of the first steady-state solution was given in the March 1 final report. There it was shown (Fig. 12 in that report) that a conserved amount of positively-charged impurity would be entirely drifted to

the Si under hot-bias with field plate positive. This case of V>O, had been shown also by Collins.[3] This is not what our experiments with radioactive Na show, however.

As indicated above, we investigated the case where immobile anion which could combine with cation was present within the oxide. This solution could account for the experimentally-observed distributions, by appropriate choice of boundary conditions.

Our experiments with radioactive cation and anion show that, at sufficiently high temperature, both are mobile. Therefore case (3), above, was examined. Experiment shows that Na and Br both tend toward roughly U-shaped distributions across the oxide. On the other hand, theory requires that the product $[Na^+][Br^-]$ be constant unless there is association and dissociation between the ions.

The following summarizes the ideas which have come out of this work:

## COMPARISON OF THEORY WITH EXPERIMENT

Experimental data on impurity distributions $N(x)$ are available for thermal oxide on Si.

Caution must be used in comparing theory to experiment because (1) the experiments are not necessarily steady-state. The air or M/O interface may act as a rate-limited source so that the total amount of impurity is not conserved as assumed. (2) Theory and experiment do not include all mobile species, particularly water species, which are present in the oxide. (3) Thermal oxide on Si is not homogeneous, as assumed, but is oxygen-rich toward the air interface. (4) Contact potential difference should be included since it can be of the order of $V_c$.

1. Pile-up of Na in the oxide at the Si results from straight-forward image-charge force. (This is in addition to any segregation effect that

might exist between the oxide and the oxide/Si interface "phase"). This is supported by the fact that pile-up is accompanied by electrical MOS shifts which are also due to negative charge in the Si surface. Fig. 3 shows Na distribution in "clean" oxide in which there is no pile-up and no MOS flat-band voltage offset ($\Delta V$) due to impurities. Fig. 4 shows a drifted oxide which shows pile-up and a -50 volt $\Delta V$.

2. <u>Most Na in the oxide is effectively neutral.</u> The evidence for this conclusion is as follows:

a. No Na pile-up in the oxide would remain at the M/O interface after in-drift if all Na were Na$^+$, since $V \gg V_c$ as discussed in Model 1.

b. Reverse drift of Na-contaminated oxide with $|V| \gg V_c$ does not affect the distribution $N(x)$ except at the $SiO_2$/Si interface (Fig. 4).

c. Negative charge induced in the Si surface calculated from integrated Na concentration is always greater than that measured electrically by MOS[4, 5]. This is shown in Figs. 3, 4, 5.

d. Etch-down experiments[6] suggest that impurity charge that is responsible for Si surface potential shifts is localized within the oxide <500 Å from the Si.

e. Radiochemical diffusion and drift[4, 5, 7] data often show a pronounced dip in $N(x)$ close to the region of pile-up at the Si. This may be the transient $N(x, t)$ due to diffusion of Na across the oxide followed by electron transfer near the Si, resulting in drift of Na$^+$ to the Si interface. Note in Fig. 4 this is seen. This may be a measure of the distance before retrapping of a Na$^+$ in the $SiO_2$ near the interface.

i.    High concentrations ($\approx 10^{19}$ cm$^{-3}$) of Na contamination diffused in oxide do not show the expected U-shaped profile predicted by theory (see reference 5) but a flatter profile, as might be expected from near steady-state diffusion, plus a pile-up component at the Si inter-face.

3.    <u>Na may be in steady-state association/dissociation with negative charges.</u>    Experiments with NaBr contaminant have shown Na diffusion is followed by Br diffusion (Fig. 5) until electrical steady-state is achieved. PN = [ Na$^+$] [ Br$^-$] = constant is not observed but is expected from steady-state theory of diffusion and drift with no NaBr association.    The theoretical results of Model 2 and Model 3 suggest that association/dissociation is occurring which causes [ Br ] to be large in regions where [ Na ] is large, as is observed.

DISCUSSION

The implication of the theory compared with experiment is that most of the Na in conventional thermal oxide on Si is neutral, perhaps associated with less mobile anionic species, and that when Na$^+$ appears at the Si interface it induces image charge in the Si.

This model may be used to understand <u>kinetics</u> of Na in MOS hot-bias experiments, where it is observed that in-drift flat-band voltage shift presumed due to Na$^+$ ions (i. e. metal positive) is relatively slow, out-drift fast[7]. Slow in-drift is due to diffusion, dissociation, drift, and reassociation; charge build-up at the Si being due to Na transit across the oxide, mobility being that expected from conductivity data.    That is, a rough value of $\mu$ at $140^\circ$C obtained from a 5 min. observed in-drift time across 5000Å of oxide with +50v applied is, $\mu = x_o^2/tV = 10^{-13}$ cm$^2$ v-sec, in agreement with mobility obtained from conductivity of fused quartz attributed to a few ppm Na[8].
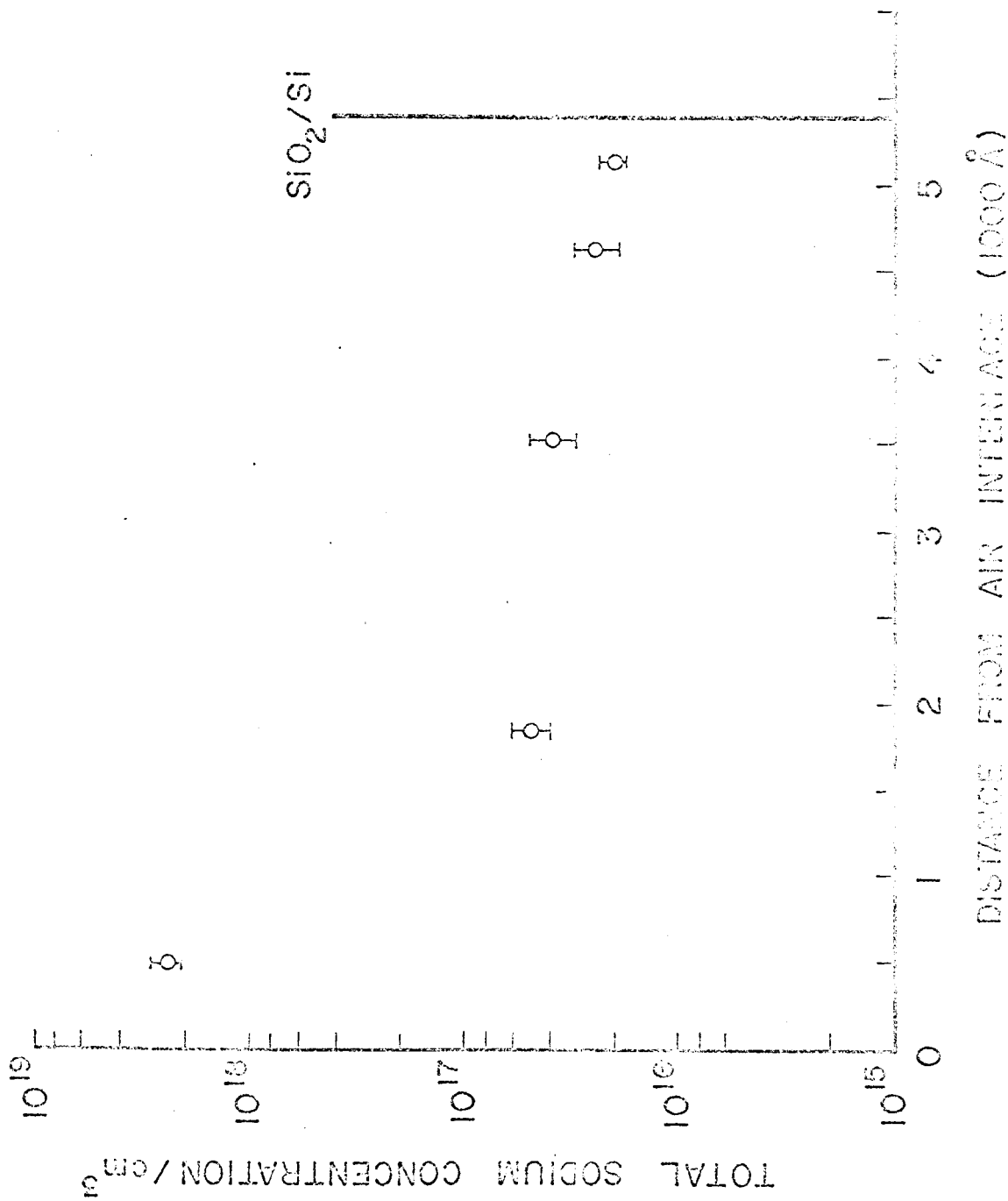
Fast out-drift is due to removal of the Na$^+$ pile-up at the Si interface.    This step is pure drift, not rate-limited by diffusion or dissociation.    The induced charge in the Si disappears as the Na$^+$ is removed to neutralizing sites in the bulk oxide.

evidence that bulk dissociation-association is controlling in-drift of Na is seen in Fig. 4 where neutral Na is distributed throughout oxide after drift. Out-drift is seen in the Fig. to consist mainly of removal of Na pile-up. These kinetics have been studied in more detail [7] by combined MOS electrical/radiochemical analysis and it is found that, while out-drift electrical recovery after in-drift is rapid, times of the order of in-drift times are required to remove completely the Na spike from the Si interface. This could lead to "apparent" complete electrical recovery after a short out-drift vs. "true" recovery after a long out-drift.

With this model, results reported by Hofstein [9] may be interpreted as Na drift, since hot-bias kinetics of Na and those observed by Hofstein are similar. In his interpretation, fast out-drift across the oxide is regarded as characteristic of the impurity species, whereas relatively slow in-drift is attributed to rate-limiting generation out of traps at the metal/ oxide interface.

Hofstein's data are in good agreement with our model. (1) Voltage dependence of in-drift and out-drift is not symmetric as might be expected from ion transit from one side of oxide to the other. Out-drift is very sensitive to small voltage, in-drift is less voltage-dependent and requires larger voltage to be comparably affected. (2) In-drift kinetics are variable, evidently sensitive to the state of the oxide, while out-drift kinetics are very reproducible, (3) "True" vs. "apparent" electrical recovery is observed.

The dependence of in-drift of Na on the state of the oxide is interpreted as due to the effect of trapping and neutralization of $Na^+$ in transit. Thus the MOS drift effects due to water species [9] and organics [10] may be, in large part, alteration of oxide Na trapping characteristics.

SiO$_2$/Si

DISTANCE FROM AIR INTERFACE (1000 Å)

TOTAL SODIUM CONCENTRATION/cm$^3$

10$^{19}$
10$^{18}$
10$^{17}$
10$^{16}$
10$^{15}$

0  1  2  3  4  5

Residual Sodium, N(x) found by neutron activation in thermal oxide on Silicon grown conventionally in wet oxygen (from reference 5). This "clean" oxide shows $4 \times 10^{11}$ negative charges per cm$^2$ by MOS analysis induced in the Si surface. Note no evidence of pile-up at the Si.

Fig. 4
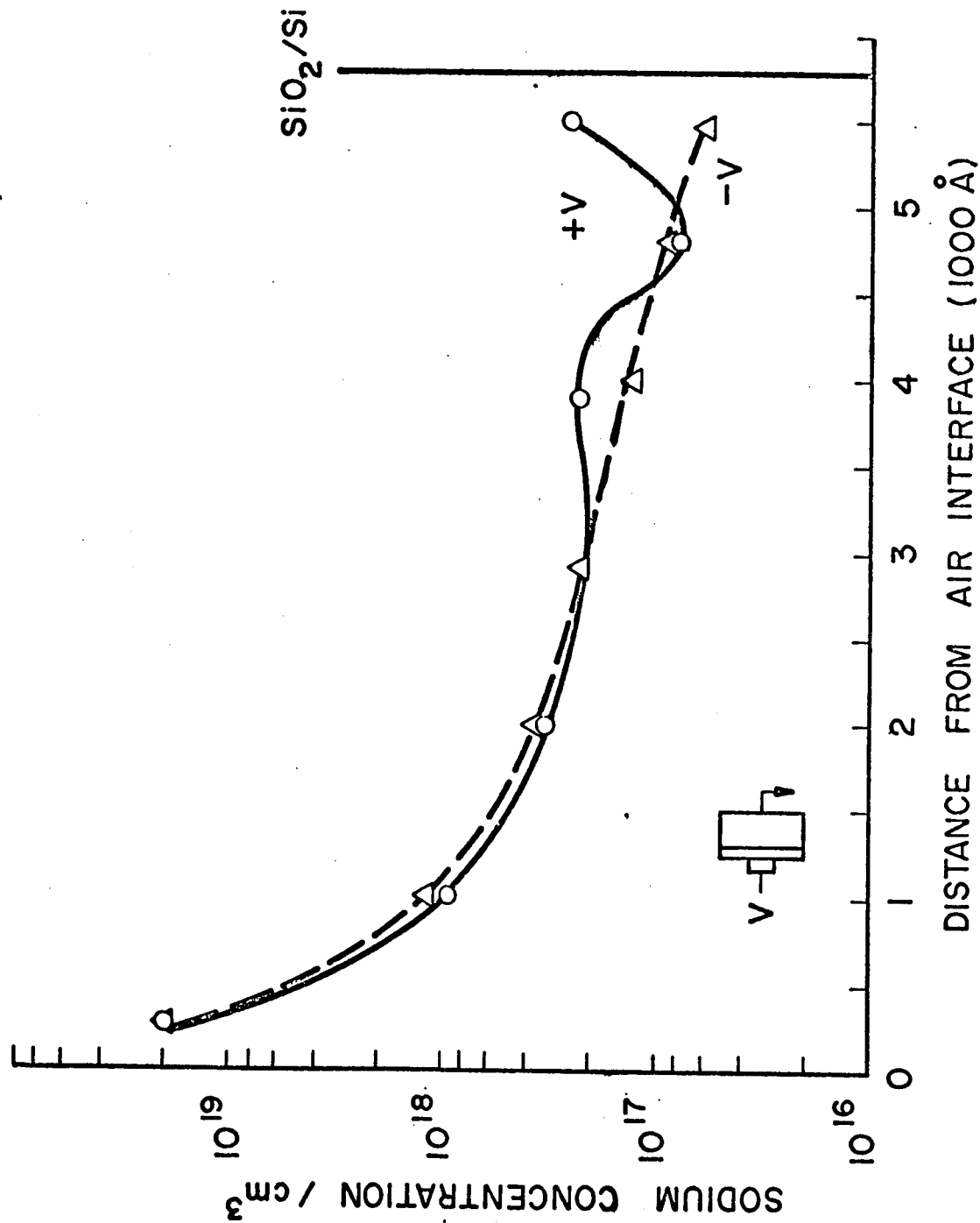
Radiotracer $Na^{24}N(x)$ from drift of $Na^{24}Cl$ in thermal oxide on Silicon (from reference 5). Two different samples. +V(in-drift) was after 15 min. at 140°C with V = +29V. -V curve was obtained after +V for 15 min. at 200°C, then -V for 15 min. at 140°C. After +V, $\Delta N_{MOS} = 2 \times 10^{12}$ cm.$^{-2}$. After -V, $\Delta N_{MOS} = 3 \times 10^{11}$ cm.$^{-2}$. $V_c$ for this case is $\lesssim$ 1V
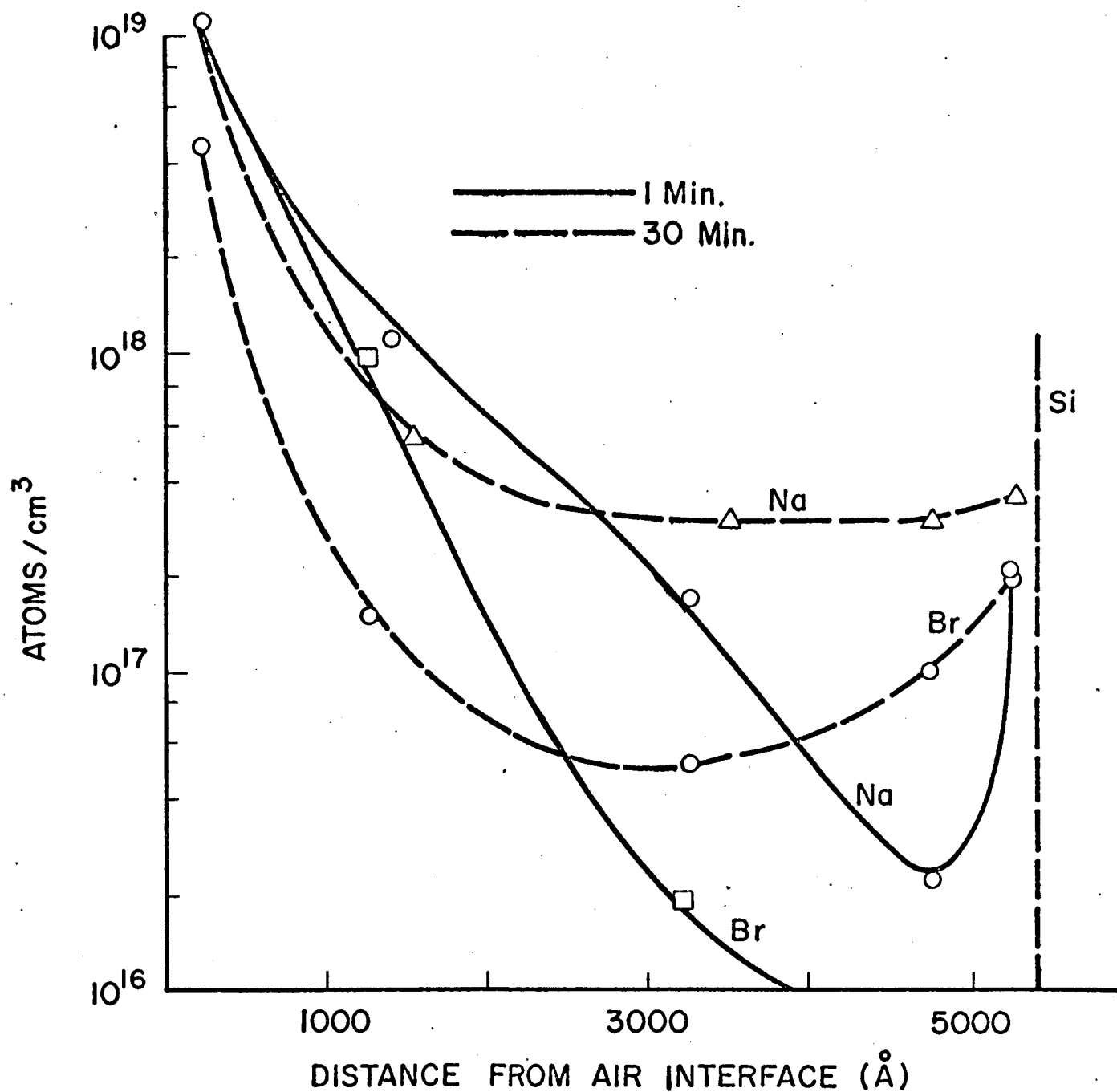
Radiotracer Na[24], N(x), and Br[82], P(x), diffusion at 800°C in thermal oxide on Si. Two different samples (from reference 7) MOS measurements gave (in units of $10^{12}$ cm$^{-2}$) after 1 min., $\Delta N = 4.6$ compared to integrated impurity (from the data shown here) inducing charge in the Si surface of 6.2. After 30 min. $\Delta N = 0.8$ compared to 1.7 integrated from these data.

Fig. 5

## Hydration of Thermal Oxide on Si (G. Holmberg and J. Hoel)

Moisture contributes to instability in MOS devices. To understand this effect quantitatively, an apparatus has been constructed to expose an oxide film on silicon to water vapor under equilibrium conditions. Vapor pressure of water and temperature of silicon substrate are carefully controlled.

Capacitance-voltage measurements are made on the sample after various times of hydration. It is expected that flat-band voltage shifts correlate with amount of hydration. Initial measurements indicate that the small flat-band voltage offset, seen with an initially clean and dried oxide, becomes even smaller after hydration at around $200^{\circ}C$.

Much effort has been expended in trying to find a suitable probe which would allow C-V measurements on a sample without removing it from the hydration cell. Mercury held in a teflon sleeve and soft gold have not been successful. It has recently been decided to remove the samples from the cell and evaporate on contacts for measurements.

In a short time, profiling measurements will be started with radio-actively-tagged water in an attempt to correlate electrical measurements with actual "water" distributions in the oxide film.

## Gold in $SiO_2/Si$ (C. Slabinski and E. Yon)

The presence of gold in the bulk depletion region of an MOS capacitor should compensate the bulk impurity doping and result in an increased depletion layer width and hence a lower capacitance minimum of the C-V curve.

The above experiments brought to light the fact that evaporated metal contacts are necessary for reproducible C-V measurements, especially of the capacitance minimum. Probe contacts give erratic data and often yield curves that do not match theory. In the present work, aluminum dots on the oxide, and gold metal on the back proved satisfactory.

Initial experiments with radiotracer $Au^{198}$ show that the gold will replate back onto the silicon from the etching solution. A subsequent soak in aqua regia removes the replated gold and the activity of the combined etchant and soaking solutions gives the true number of gold atoms in the section within 10%.

Over 50 samples have been run with radioactive gold during this quarter.

## Personnel

During the summer for 10 weeks two summer research fellows are assisting in this research. Mr. E. Greenstein is supported by the National Science Foundation and Mr. J. Hoel is supported by other research funds.

Mr. W. W. Smith Jr. has graduated with the degree of M.S. from Case. Other personnel on the grant are unchanged.

## Experimental Equipment and Techniques

1. A CVC CVE-20 vacuum evaporator has been installed, which is available for this research.

2. A probe set-up which is capable of maintaining samples at $77^{\circ}K$ in dark has been built and incorporated in the C-V plotting system.

## PUBLICATIONS

March 1-3      "Ion Drift in MOS-Experiment and Theory", A. B.
Kuper, Silicon Interface Specialists Conference,
Las Vegas, Nevada

April 19-22     "Combined MOS and Radiochemical Analysis of
Impurities in $SiO_2$ on Si", A. B. Kuper, *European
Semiconductor Device Research Conference,
Bad Nauheim, Germany.

May 7-12      "Theory of Charge Distribution in MOS Oxide"
H. P. Caban-Zeda and A. B. Kuper, Electrochemical
Society, Dallas.

Theses:

M. S. Electrical Engineering, W. W. Smith, Jr.
June 1967. "Phosphosilicate Glass Passivation Against
Sodium Impurity in Thermal Oxide on Silicon".

M. S. Electrical Engineering, H. P. Caban-Zeda,
June 1967. "Theory of Impurity Charge in MOS
Oxide".

* NSF Travel Grant awarded for airfare.

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10. L. V. Gregor, "Solvent-Induced Polarization in MOS Devices", J. Electrochem. Soc. vol 113, p 59C (March, 1966)